

# Structure of a low-lying isomer of $\text{BOSi}_2$ , as a free-space planar cluster, using the Hartree-Fock method plus second order perturbations

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## Abstract

The Hartree-Fock (HF) method, supplemented by low-order Møller-Plesset (MP2) perturbation theory, has been utilized to predict the nuclear geometry, assuming planarity, of a low-lying isomer of the free space cluster  $\text{BOSi}_2$ . The planar structure found at equilibrium geometry is shown to be stable against small amplitude molecular vibrations. Finally, some brief comments are made on the possible relevance of the above free-space cluster geometry to the known B–O defects which limit the improvement of minority carrier lifetime in a form of *p*-type silicon.

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The main aim of this Letter is to present a theoretical study of the nuclear geometry of a low-lying isomer of  $\text{BOSi}_2$  in the form of a free-space planar cluster. As a neutral cluster, this species has, of course, spin density, and

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we have therefore paid attention also to the singly ionized cluster  $(\text{BOSi}_2)^+$ . The effect of such ionization on the equilibrium geometry of the cluster is then another important focal point. In these calculations, we have utilized the Hartree-Fock (HF) method, supplemented by second-order Møller-Plesset (MP2) perturbation theory [1]. Correlation-corrected MP2 calculations were carried out for the optimizations. All calculations were performed by means of Gaussian 09 software [2], where for the augmented correlation-consistent polarized valence only the quadruple zeta basis set [3] was used (aug-cc-pvqz).

We have taken as starting point a cluster of two free-space Si atoms, held at first at their equilibrium separation of 2.265 Å [4], as we allow B and O atoms to approach the free-space  $\text{Si}_2$  complex. The study of the interaction of the boron oxide subcluster with the silicon dimer in free space is motivated by the recent interest developed towards the formation of interstitial  $(\text{BO})_n$  impurity complexes in solid-state silicon, which have been considered in at least two distinct arrangements with respect with the surrounding crystal, and give rise to different electrical levels and vibrational spectra, depending on their orientation in the crystal [5]. Fig. 1 shows the equilibrium nuclear geometry we predict, when we restrict ourselves to planarity, for the ionized cluster  $(\text{BOSi}_2)^+$ , assuming spin compensation, and keeping the  $\text{Si}_2$  separation as in the free-space Si cluster. The remaining equilibrium bond lengths as calculated by HF theory are recorded in Å in Table 1. The effect of relaxing then finally the  $\text{Si}_2$  separation to achieve minimum energy is shown in Table 1, the difference in energy due to such final relaxation being extremely small, as shown in Table 1.

Table 2 then records the final relaxed cluster geometry for the neutral case of  $\text{BOSi}_2$ , again, however, with planarity assumed. The relatively small changes in the equilibrium bond lengths due to ‘charging’ is clear from comparison between Tables 1 and 2.

Tables 1 and 2 show, together with Fig. 1, the rather remarkable property that the atoms 1, 2, and 4 form an almost equilateral triangle, with the O atom bonded directly to B, with bond length 1.22 Å. In this context, we also record in the two Tables the dipole moments for both neutral and ionized clusters. Fig. 2 shows the HOMO orbitals of the two clusters, while Table 3 reports the NBO charges of the two clusters.

Potential energy surfaces (PES) were evaluated for both neutral  $\text{BOSi}_2$  and singly ionized  $(\text{BOSi}_2)^+$  (Fig. 3). To this aim, we have maintained the same basis set as in the structural calculations, but applying the PBE functional for the neutral cluster, while PBE1 was adopted for the charged sys-

tem, since convergence criteria are not met with PBE. We have explored the PES in a range of the Si–B distance  $R = 2.06 - 2.18$  Å, with the angle  $\theta = \angle \text{Si, B, Si} = 52 - 66^\circ$ . Fig. 3 shows that, in strong agreement with MP2 calculations, absolute minima are found for  $R \simeq 2.10$  Å,  $\theta \simeq 60^\circ$  for the neutral cluster, and  $R \simeq 2.12$  Å and  $\theta \simeq 60^\circ$  for  $(\text{BOSi}_2)^+$ .

We have also studied the frequencies of the normal modes of vibration for both the charged and neutral clusters (Table 4). All the frequencies are real, which implies the stability of both clusters against small vibrations.

Finally, for the neutral planar cluster  $\text{BOSi}_2$ , with its structure as recorded in Table 2, the cluster energy for this low-lying isomer is recorded in Table 4. The energy required to separate the above planar clusters into its free-space neutral atoms is of 0.5981 Hartree for the neutral cluster, and of 0.5663 Hartree for the singly ionized cluster.

In relation to the above predictions, it would, of course, be interesting if experiments could be carried out on such clusters of  $\text{BOSi}_2$  as are studied here, to ascertain whether our predicted planar nuclear geometries are among the low-lying isomers of such species.

But, in the absence, to our knowledge, of such experiments, we shall have recourse below to some recent theoretical work by Chen *et al.* [6], which, however, deals with the structure of boron-oxygen defects in a form of *p*-type silicon crystal (see also [5]).

To summarize briefly, the main achievements of the present theoretical study are the HF-MP2 bond lengths shown for the planar clusters of  $\text{BOSi}_2$  in Tables 1 and 2, corresponding to the singly ionized and neutral free-space clusters, respectively. While no experimental results on such free-space clusters seem to be available presently, some contact can be made with available theoretical work on BO defects in a particular *p*-type silicon crystal. In the latter solid-state assembly, the Si–B distance of 1.90 Å is shown in Fig. 1(a) of Ref. [5], while 2.07 Å is recorded in their Fig. 1(b). Our Table 2 predicts the cluster Si–B length as 2.1 Å, which is already in excellent accord with the above values.

As mentioned earlier, we believe, in view of our present predictions, that experiments on free-space clusters  $\text{BOSi}_2$  would now be of interest.

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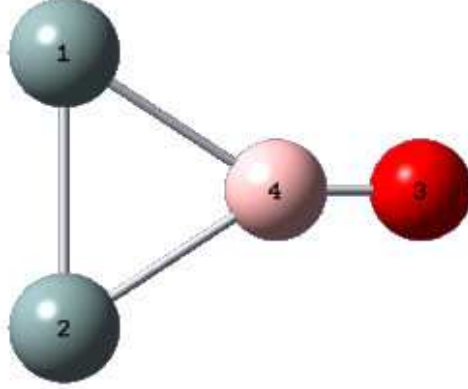


Figure 1: (Color online.) Equilibrium structure for the spin compensated, ionized cluster  $(\text{BOSi}_2)^+$  (1, 2: Si; 3: B; 4: O). We assume planarity and keep the  $\text{Si}_2$  separation as in the free-space Si cluster. See Table 1 for more structural details.

	Si-Si free	Si-Si fixed
$E$ (a.u.)	-677.7901	-677.7847
dipole (Debye)	6.38	6.66
symmetry	$C_{2v}$	$C_{2v}$
1-2 ( $\text{\AA}$ )	2.11	2.26
1-4 ( $\text{\AA}$ )	2.11	2.13
2-4 ( $\text{\AA}$ )	2.11	2.13
3-4 ( $\text{\AA}$ )	1.22	1.22
$\angle 1,4,2$ ( $^\circ$ )	59.83	64.08
$\angle 1,2,4$ ( $^\circ$ )	60.09	57.96

Table 1: Predicted structural details for  $(\text{BOSi}_2)^+$  in the equilibrium geometry, as shown in Fig. 1. Both columns refer to a planar geometry, but with free Si-Si distance (first column), and Si-Si fixed as in the free-space  $\text{Si}_2$  cluster (second column), *i.e.* 2.2648  $\text{\AA}$  [4].

	Si-Si free	Si-Si fixed
$E$ (a.u.)	-678.1352	-678.1273
dipole (Debye)	4.41	4.3
symmetry	$C_{2v}$	$C_{2v}$
1-2 ( $\text{\AA}$ )	2.12	2.26
1-4 ( $\text{\AA}$ )	2.1	2.11
2-4 ( $\text{\AA}$ )	2.1	2.11
3-4 ( $\text{\AA}$ )	1.22	1.23
$\angle 1,4,2$ ( $^\circ$ )	60.71	64.73
$\angle 1,2,4$ ( $^\circ$ )	59.64	57.64

Table 2: Predicted structural details for neutral cluster  $\text{BOSi}_2$  in the equilibrium planar geometry. The energies of the isolated atoms are  $-288.961$  a.u. (Si),  $-75.0056$  a.u. (O),  $-24.6016$  a.u. (B), yielding a total energy difference of 0.5981 a.u. of the isolated atoms, with respect to the ground-state energy of the neutral cluster  $\text{BOSi}_2$  (estimated with fixed Si-Si distance).

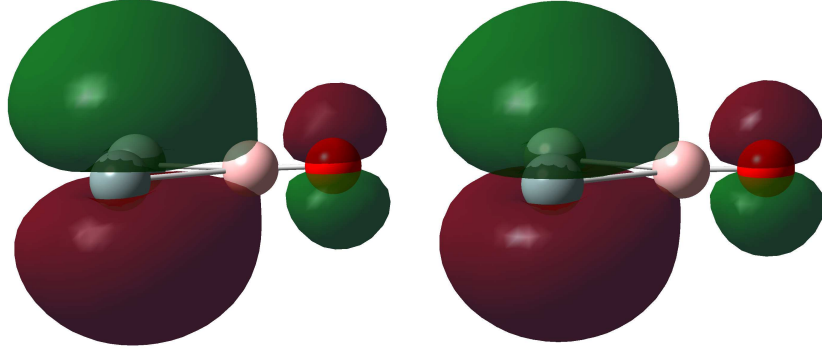


Figure 2: (Color online.) HOMO orbitals of the neutral (left panel) and charged cluster (right panel).

$i$	$\text{BOSi}_2$	$(\text{BOSi}_2)^+$
1	0.238	0.755
2	0.238	0.755
4	0.412	0.234
3	-0.888	-0.743

Table 3: NBO charges on the  $i$ th atom of neutral and singly ionized  $\text{BOSi}_2$  cluster, with free Si-Si distance.

BOSi <sub>2</sub>	(BOSi <sub>2</sub> ) <sup>+</sup>
180.89	140.75
338.13	385.18
394.85	387.96*
584.95	391.41
628.56*	559.93
1793.73	1819.81

Table 4: Vibrational frequencies (in  $\text{cm}^{-1}$ ) of normal modes of neutral and singly ionized BOSi<sub>2</sub> cluster, with free Si-Si distance. In particular, frequencies labelled with \* refer to out-of-plane normal modes.

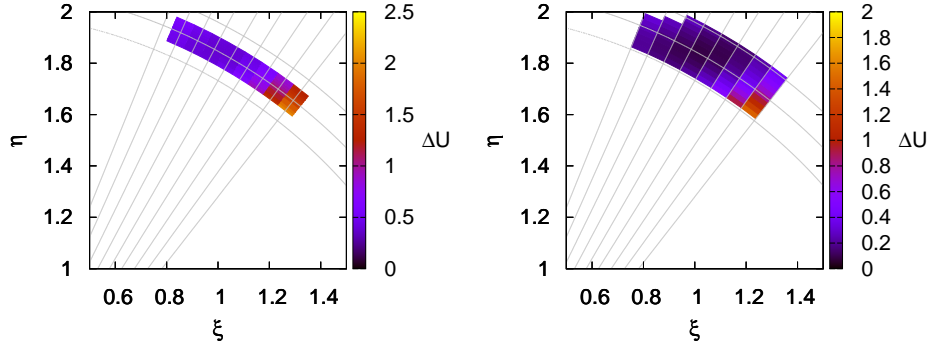


Figure 3: (Color online.) Contour plots of the potential energy surfaces for neutral BOSi<sub>2</sub> (left panel) and singly ionized (BOSi<sub>2</sub>)<sup>+</sup> (right panel), as a function of  $\xi = R \cos \theta$  and  $\eta = R \sin \theta$ , where  $R = 2.0 - 2.2 \text{ \AA}$  is the Si-B distance, and  $\theta = 52^\circ - 68^\circ$  is the  $\angle \text{Si,B,Si}$  angle. Actually plotted is the difference  $\Delta U$  of the potential energy with respect to its minimum value, in each case. Distances are in  $\text{\AA}$ , while energies are here in eV.